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# **Low Cost SiO<sub>x</sub>-Graphite and High Voltage Spinel Cathode**

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Varennnes, QC, Canada, J3X 1S1**

**DOE-BATT Review Meeting**

**ID # ES048**

# Overview

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## Timeline

- Start date: March 2009
- End date: December 2012
- 60% completed

## Barriers

- Low energy
- Poor cycle/calendar life

## Budget

- Total Project Funding: \$1095K
- FY11 funding \$365K
- FY10 funding \$365K
- FY09 funding \$365K

## Partners

- V. Battaglia, V. Srinivasan and R. Kostecki (LBNL)
- J. Goodenough (U. Texas)
- M. Thackeray (ANL)
- C. Julien, A. Mauger (U. Paris 6)
- X.Q. Yang (BNL)

# Objectives

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- ❖ Synthesize and evaluate  $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$  as high voltage cathode material.
- ❖ Replace graphite anode with an alternative material that meets the requirement for low cost and high energy.
- ❖ Develop *in-situ* and *ex-situ* SEM and TEM techniques to analyze the SEI layer properties.
- ❖ Cell assembly of 18560 with the BATT chemistry.

# Approach

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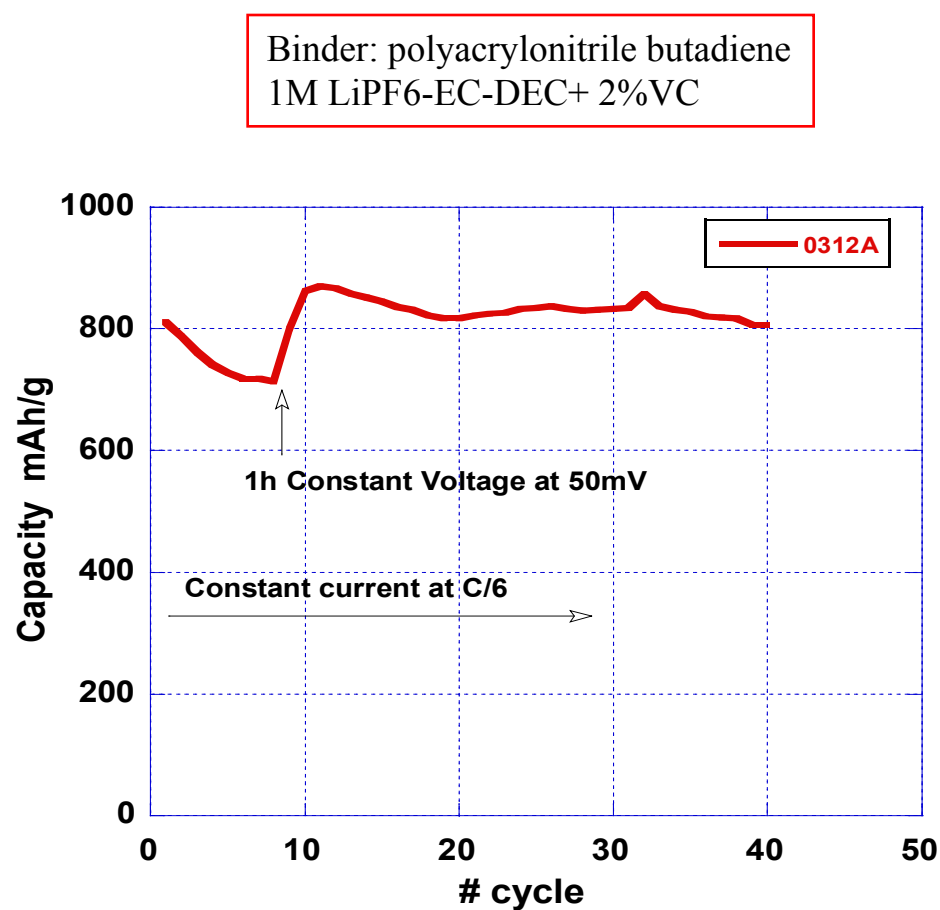
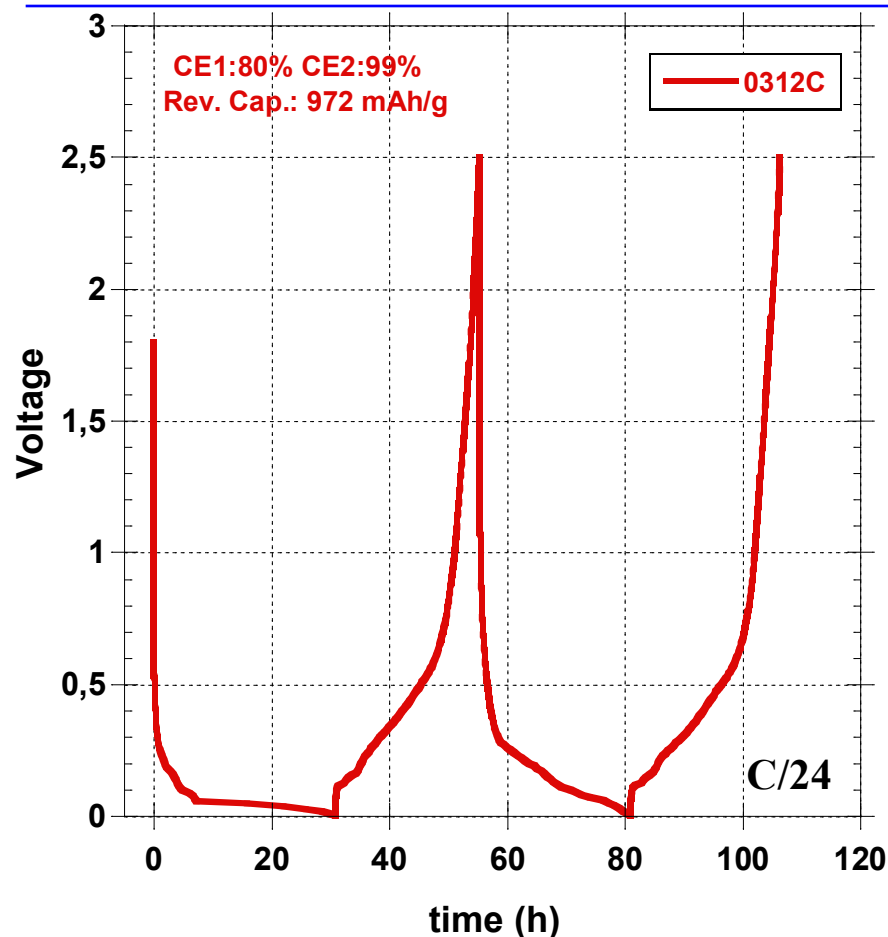
- HQ efforts in the BATT program to investigate and improve SEI layers on alternative anodes include several tasks:
  - Prepare laminate anode films and powders, and supply them to investigators in Topic 3a involved with SEI analysis using different techniques (*in-situ*, *ex-situ*).
  - Identify benefits of binder (SBR, Polyimide, EPDM) compared to PVDF in new anode and cathode materials.
- Investigate performance of high-voltage spinel cathode in laboratory cells.
  - Stabilize the  $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$  cathode by protecting its surface with more stable material to suppress the secondary reaction with the electrolyte.
  - Synthesize  $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$  at HQ and supply the optimized material to BATT investigators for evaluation.
- Utilize *in-situ* and *ex-situ* SEM and TEM to investigate the SEI layer on the anode and cathode.

# MILESTONES

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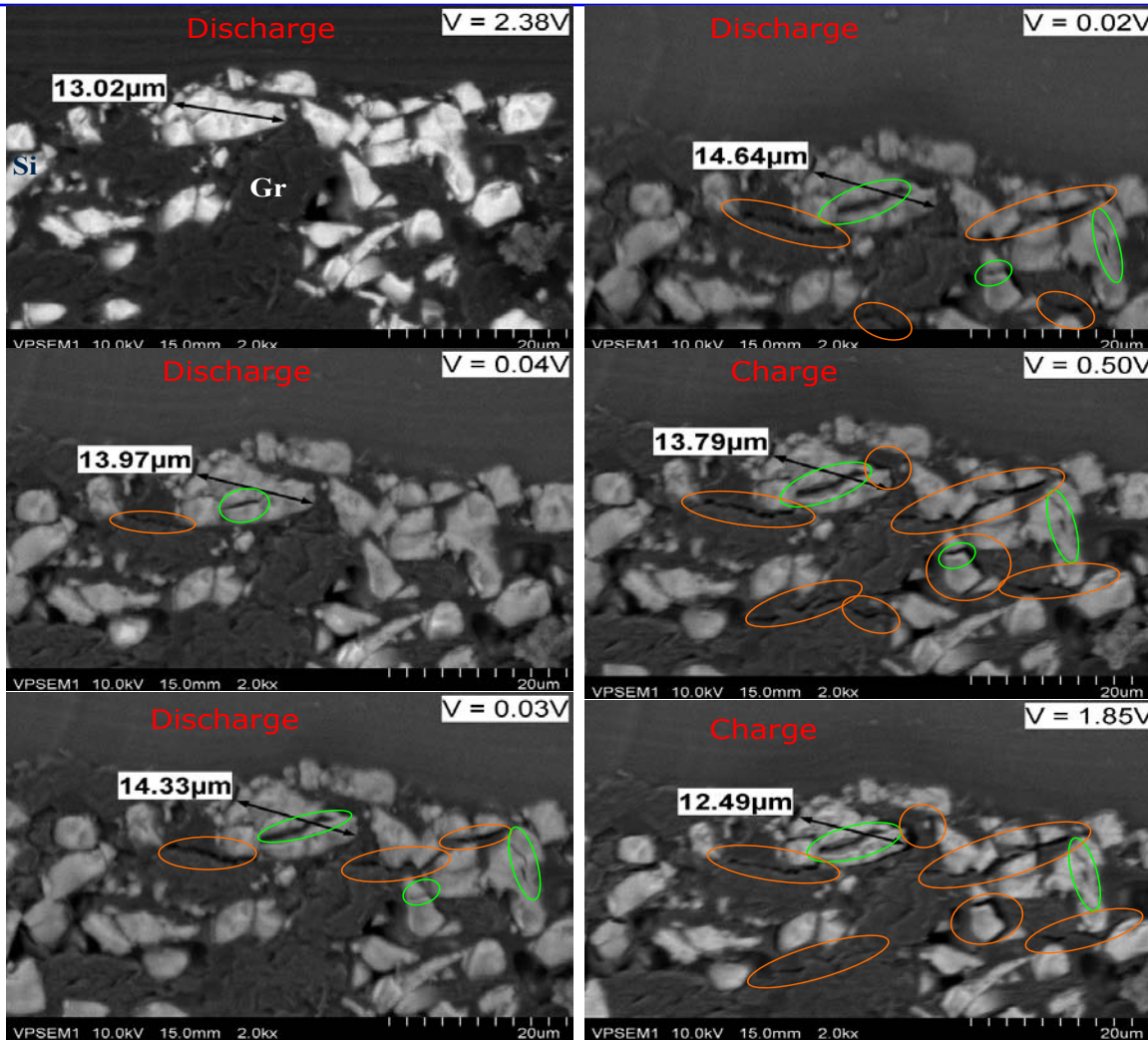
- **Completed evaluation of the effect of the binder on the  $\text{SiO}_x$  anode performance.**
- **On going**
  - **Developed process to stabilize the surface of the  $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$  cathode.**
  - **Synthesized  $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$  cathode material and supply BATT investigators.**
  - **Developed *in-situ* and *ex-situ* SEM and TEM techniques to investigate the SEI layer on the anode and the interface on the  $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$  oxide spinel.**
  - **Evaluation of 18650 cells assembled at HQ**

# (C-SiO<sub>x</sub> + Graphite (1:1)) Anode



- By using polyacrylonitrile butadiene as binder, the 1CE was 80% and the reversible capacity was 972mAh/g.
- The constant voltage step at discharged state (50mV) improves the cycling performance.

# (C-SiO<sub>x</sub> + Graphite (1:1)) Anode: *In-Situ*



Binder: Polyimide  
Discharge/Charge: C/24  
1M LiPF<sub>6</sub>-EC-DEC+2%VC

Technical Accomplishments

- The *in-situ* studies revealed that larger particles (~13μm) start to develop cracks at around 0.1V and the smaller particles (< 2μm) are more stable.
- Some fissures were observed and the particles are delaminated .

# (C-SiO<sub>x</sub>+ Graphite (1:1)) Anode: In-Situ

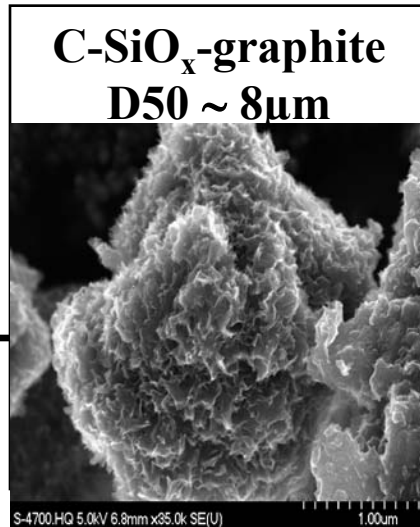
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## Movie

In-Situ SiO  
2010-07-29



# Si-Based Anode



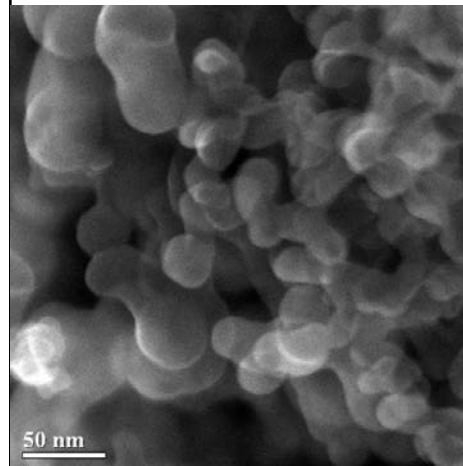
**EC1: 80%**  
**1058 mAh/g**

***In-situ SEM***

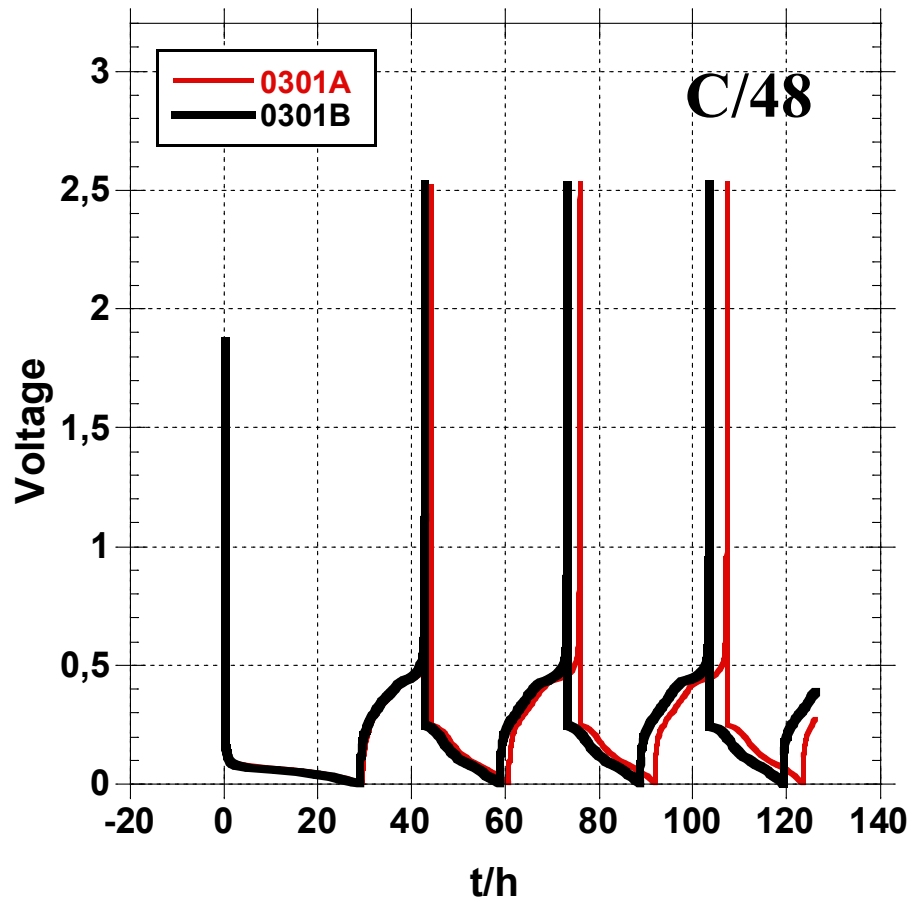
**Bigger particle (~13μm)  
cracks during the first  
discharge**

**Smaller particle is needed**

**Si nano**



# Si-Nano Material for Anode



Li coin type cell  
Binder: Polyimide  
1M  $\text{LiPF}_6$ -EC-DEC+2%VC

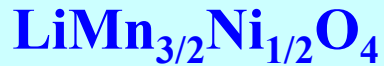
Discharge/Charge: C/48  
 $T=25^\circ\text{C}$

Cell:	0300A	0300B
EC1 (%)	50	49
EC3 (%)	96	96
Qrev (mAh/g)	1224	1153

- The reversible capacity was only 1220mAh/g for the Si-nano material at low rate:
  - Carbon coating is needed
  - *In situ* SEM studies needed to analyze low-capacity behavior.

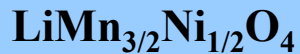
# Cathode Material Plan

## High Voltage Cathode



Charging  $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$  requires high voltage (4.9V), which could induce its degradation in performance. Protecting the  $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$  surface can minimize this side reaction.

### HQ Synthesis



Optimized material  
be will sent to the  
BATT PIs

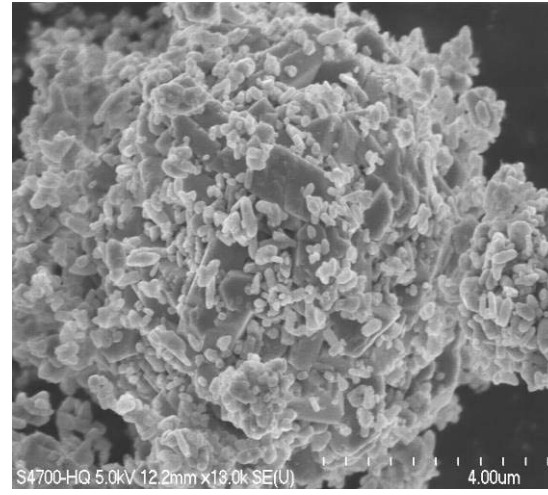
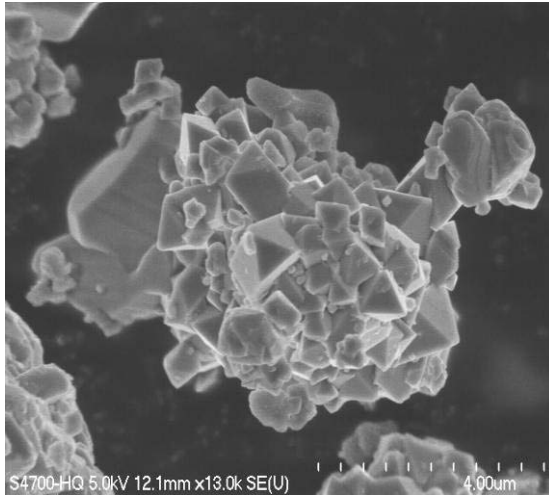
### Surface protection of LMN cathode

LFP coated LMN  
(dry process)

Oxide and ceramic LMN  
surface treatment  
(wet process)

- Ni-O  
- Mn-O  
-  $\text{LiCoPO}_4$   
-  $\text{AlPO}_4$

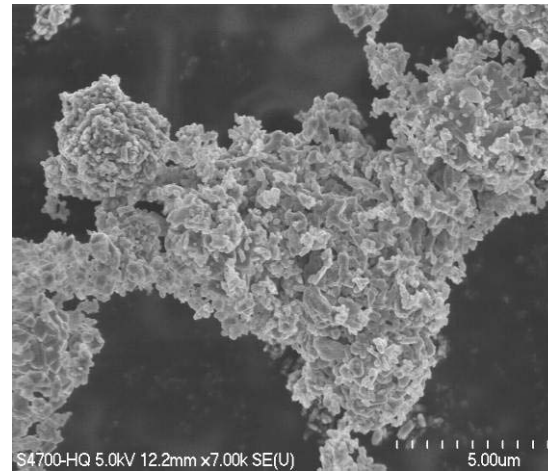
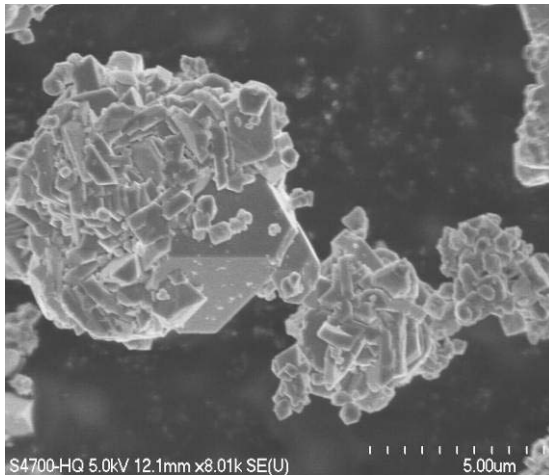
# LiFePO<sub>4</sub> Coated LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub>: SEM



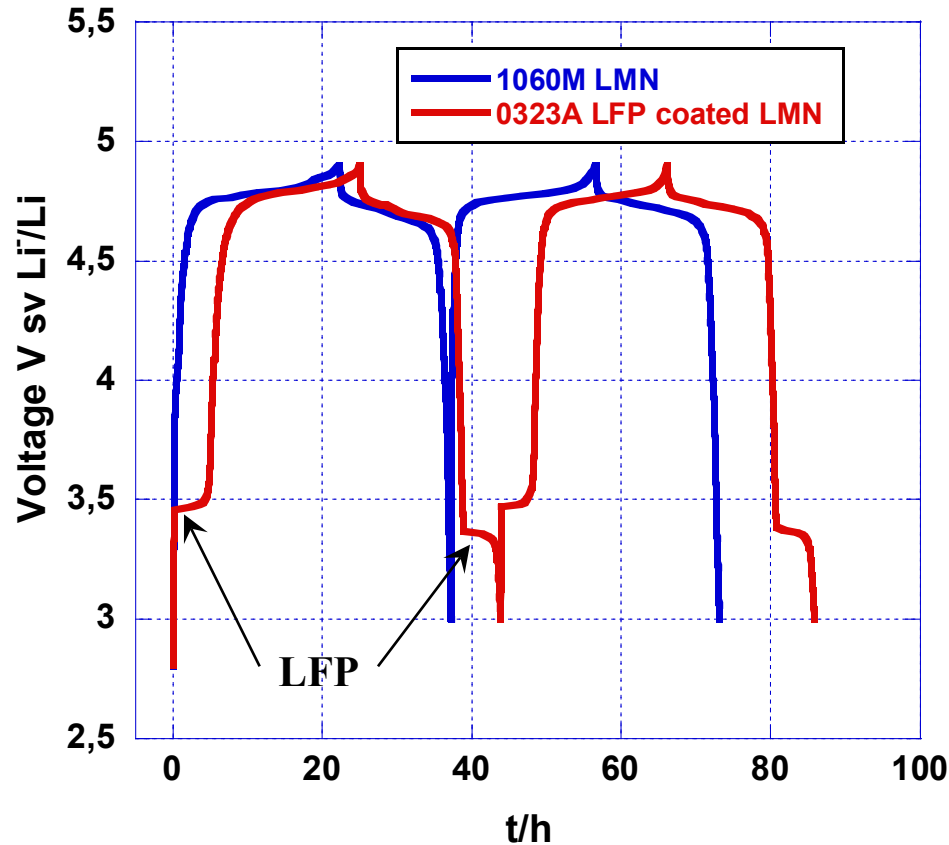
LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub>

Dry process

LFP(LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub>)



# LiFePO<sub>4</sub> Coated LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub>: Formation

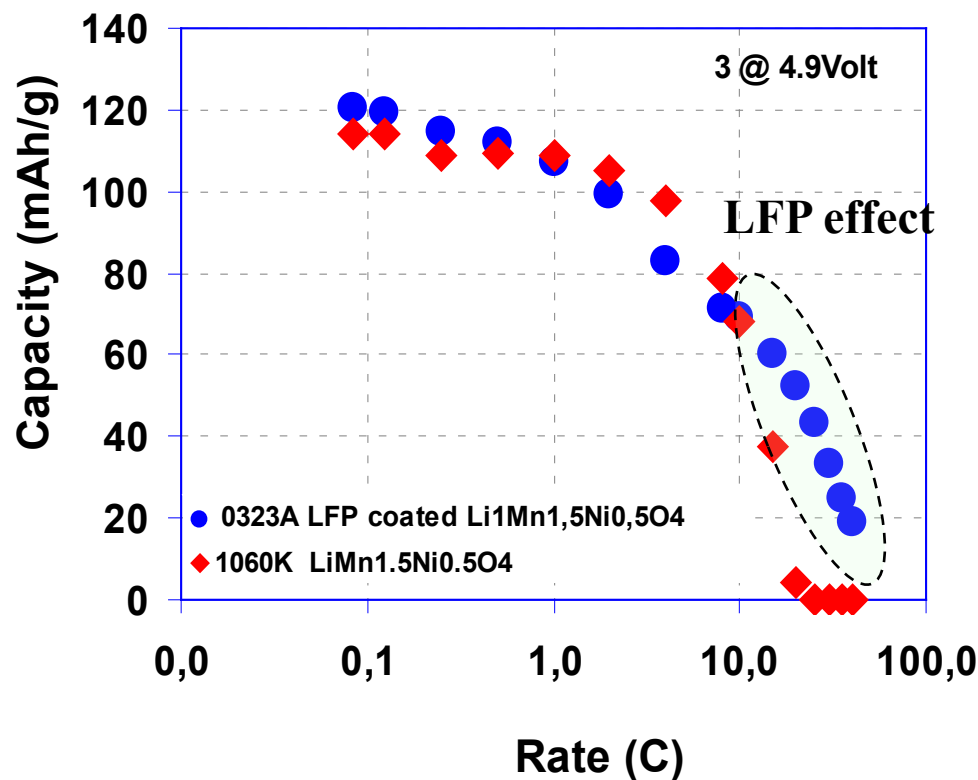


LiFP(LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub>):20(80) Wt%  
Discharge/Charge: C/24  
1M LiPF<sub>6</sub>-EC-DEC+ 2%VC

	EC1 (%)	EC2 (%)	Cap (mAh/g)
LFP coated (LiMn <sub>1.5</sub> Ni <sub>0.5</sub> O <sub>4</sub> )	76	88	123
LiMn <sub>1.5</sub> Ni <sub>0.5</sub> O <sub>4</sub>	67	86	104

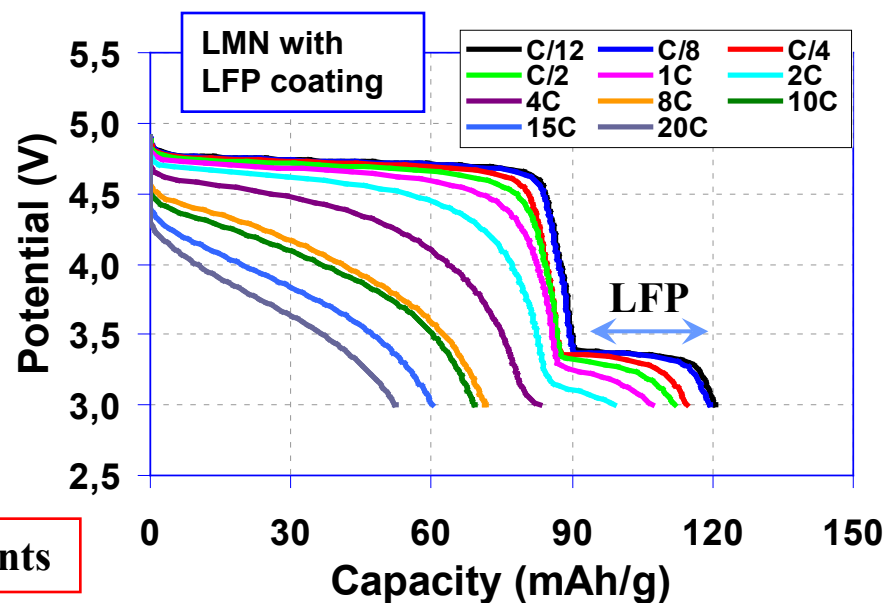
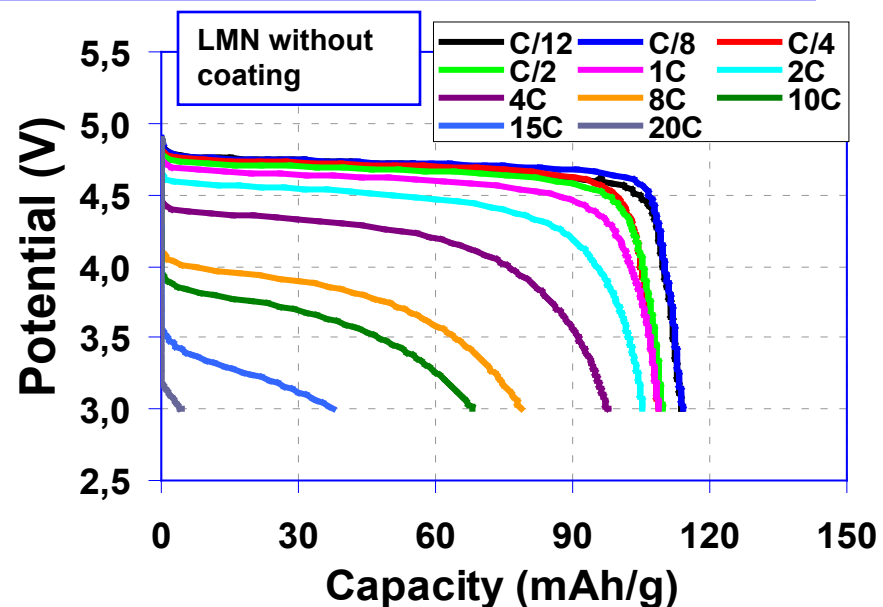
-The LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub> was successfully coated with LiFePO<sub>4</sub> using dry process.

# LiFePO<sub>4</sub> Coated LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub>: Ragone Test



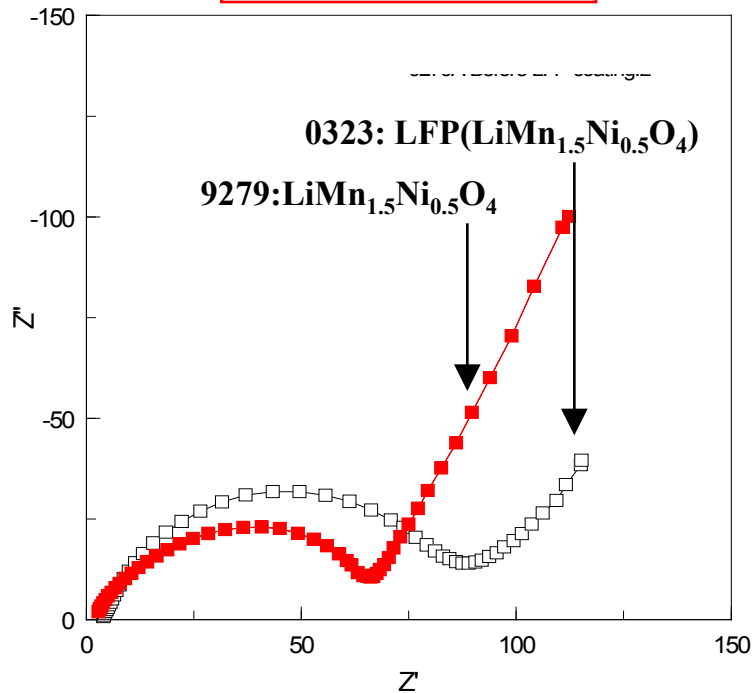
-The high power performance was improved  
With LFP-coated LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub>.

Technical Accomplishments



# LiFePO<sub>4</sub> Coated LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub>: Interfaces

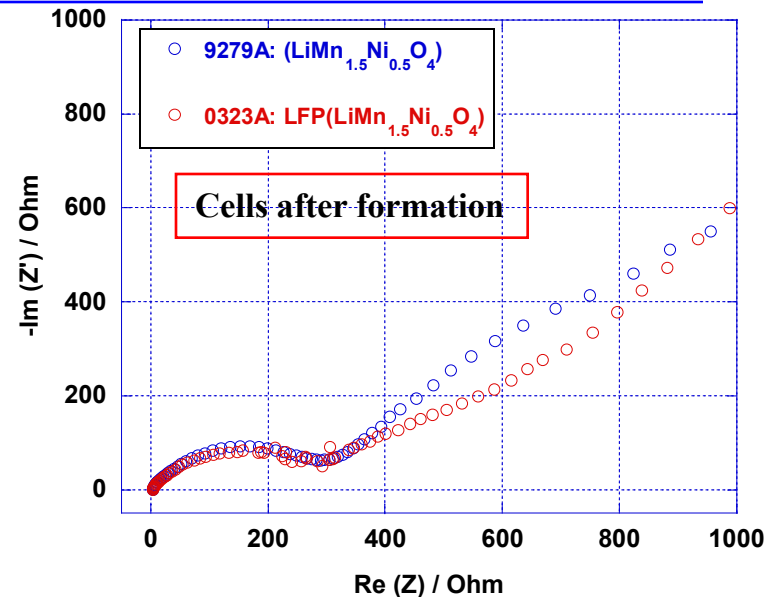
Cells before formation



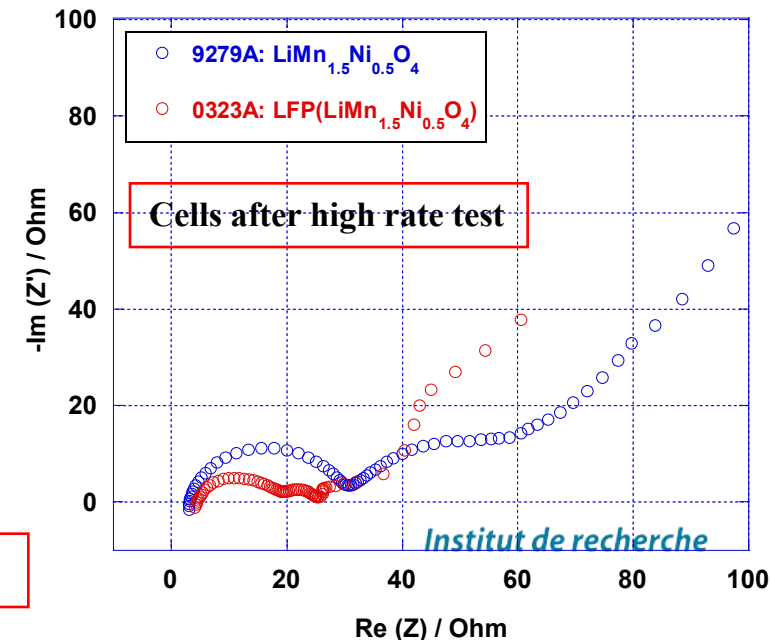
-A comparable interface was obtained after the formation cycles.  
-The interface changed after high rate test to the LFP-coated LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub>.

Technical Accomplishments

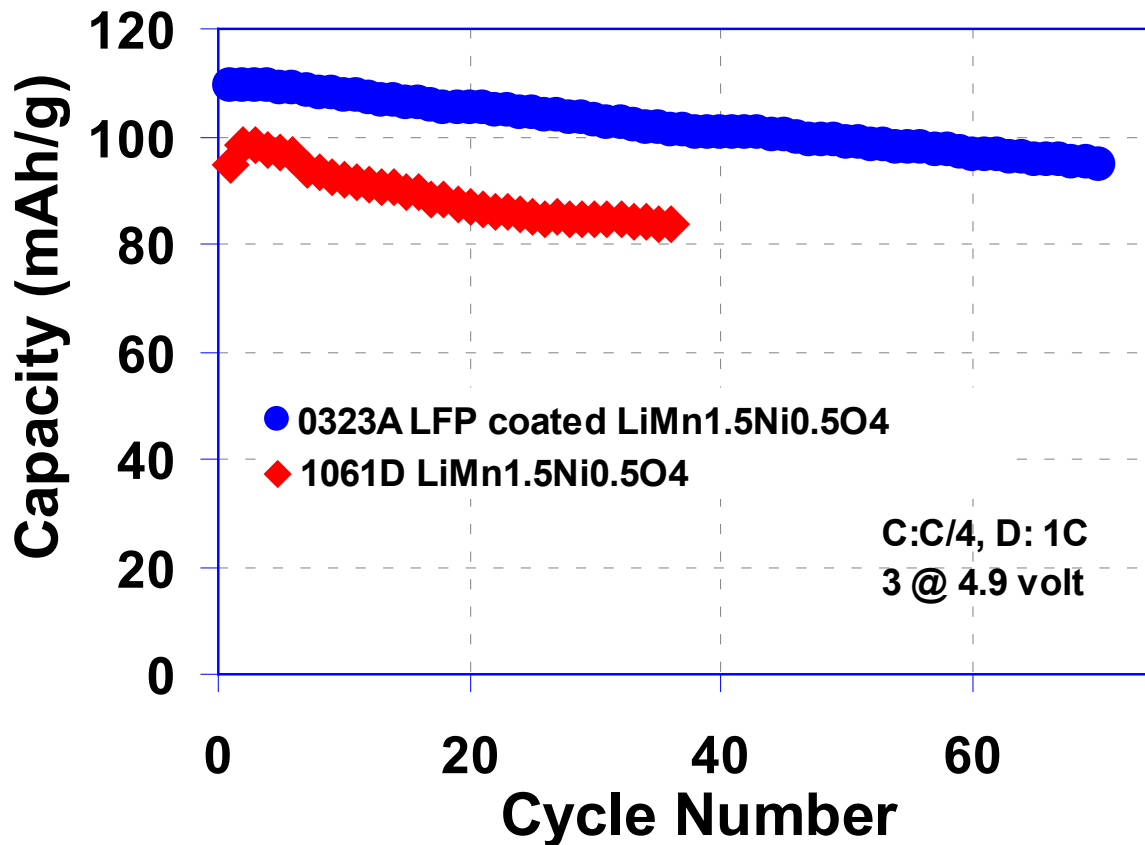
Cells after formation



Cells after high rate test



# LiFePO<sub>4</sub> Coated LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub>: Cycling



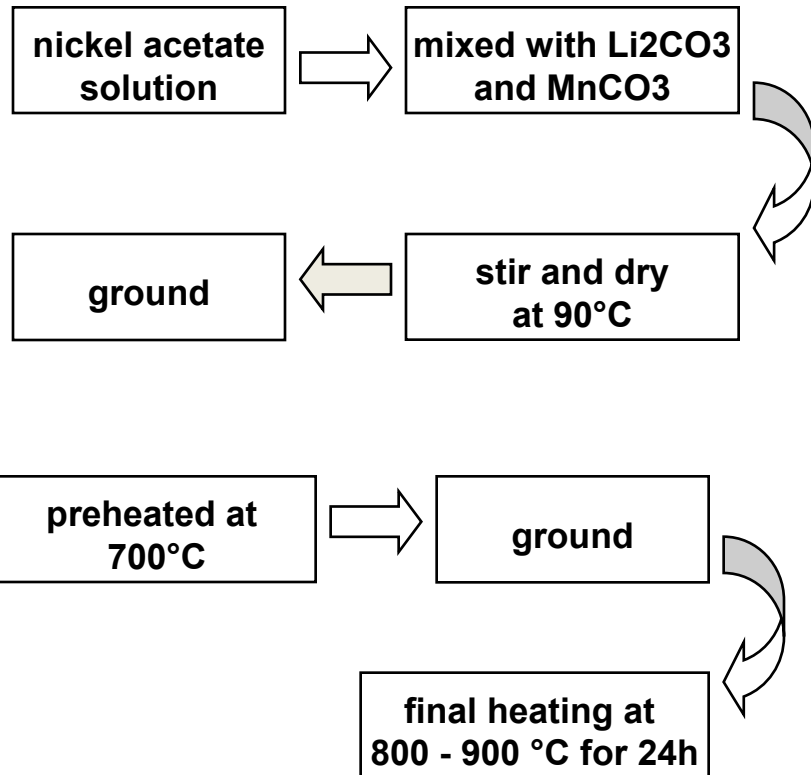
-The LFP-coated LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub> cathode showed less capacity fade (3-4.9V) cycled at 1C compared to uncoated one.

Technical Accomplishments

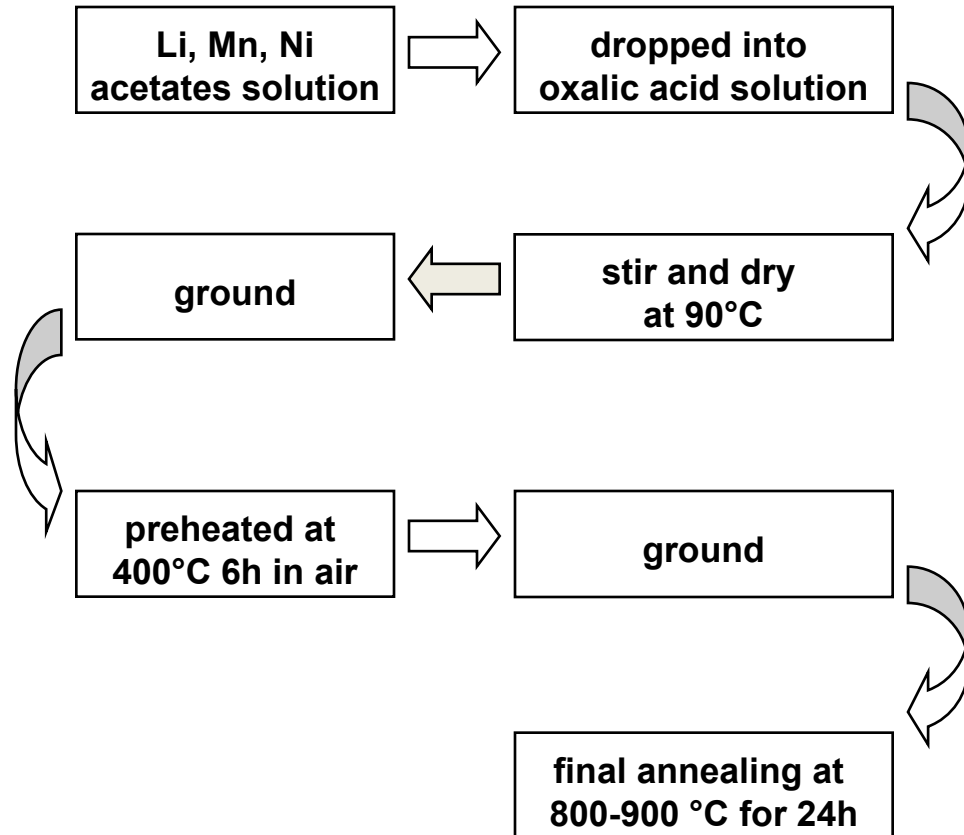


# $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$ : HQ-Synthesis

## Solid-State process (SS sample)

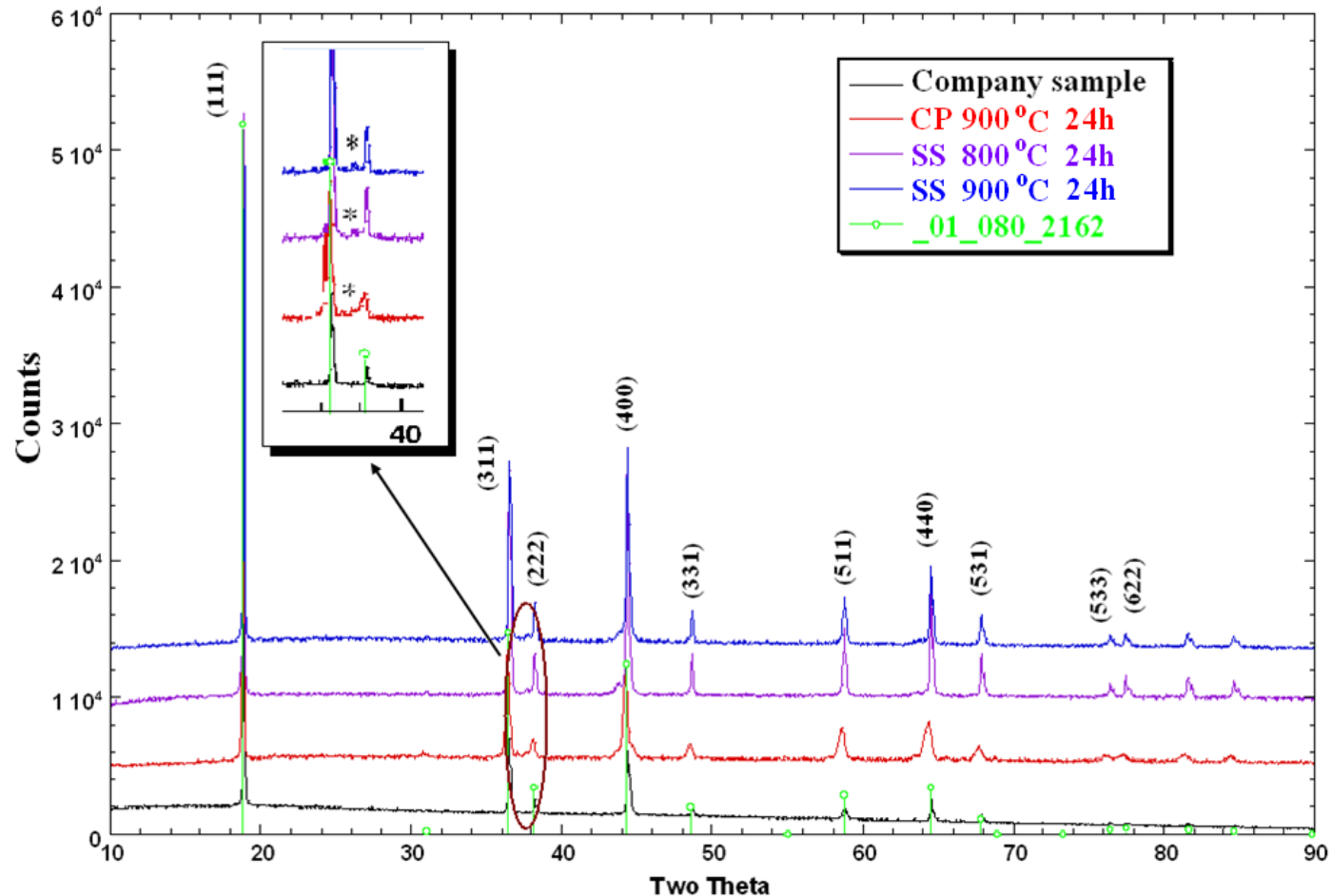


## Co-Precipitation method (CP sample)



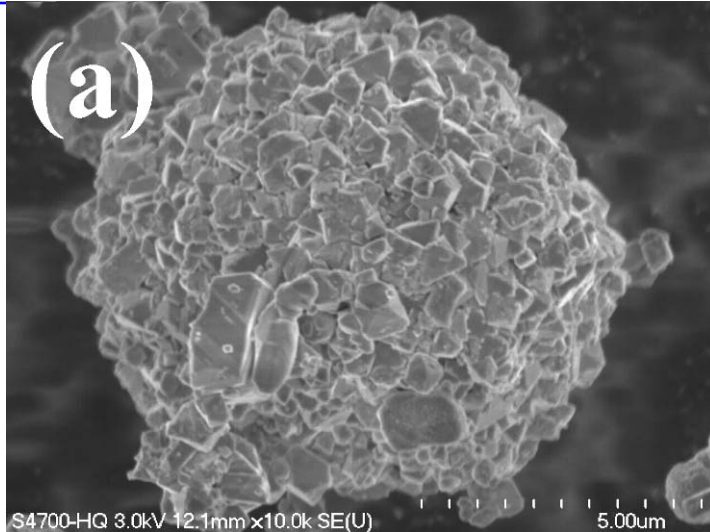
3 samples of  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  were sent to Vince Battaglia (LBNL) for evaluation.

# HQ Synthesis of $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$ : XRD

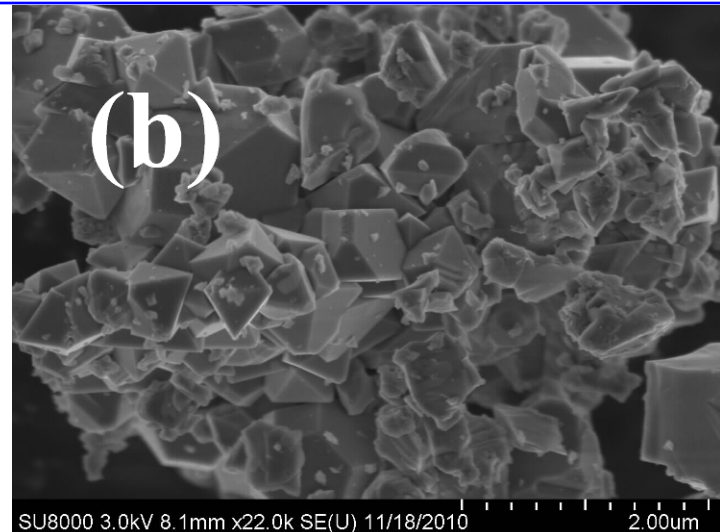


- Trace impurities ( $2\theta = 38^\circ$  and  $45^\circ$ ) were found in HQ samples, probably due to loss of oxygen and/or lithium at high temperature.
- Samples crystallize better with disordered structure at higher temperatures.

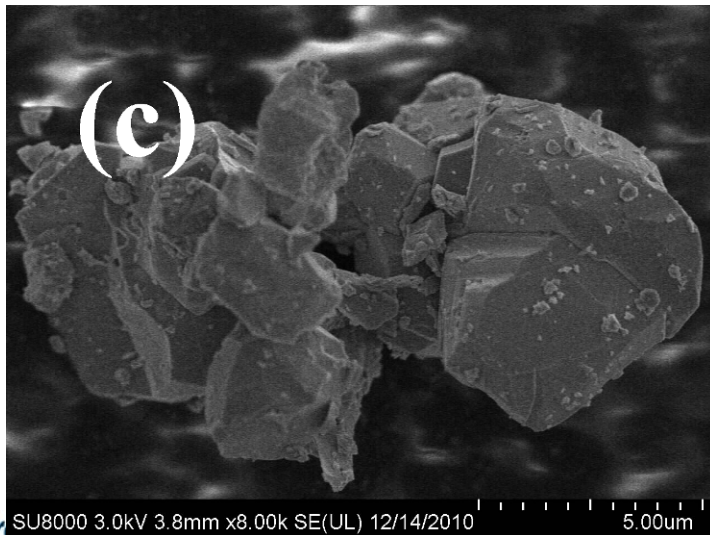
# HQ Synthesis of $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$ : SEM



(a) Company sample



(b) Co-Precipitation (CP) sample

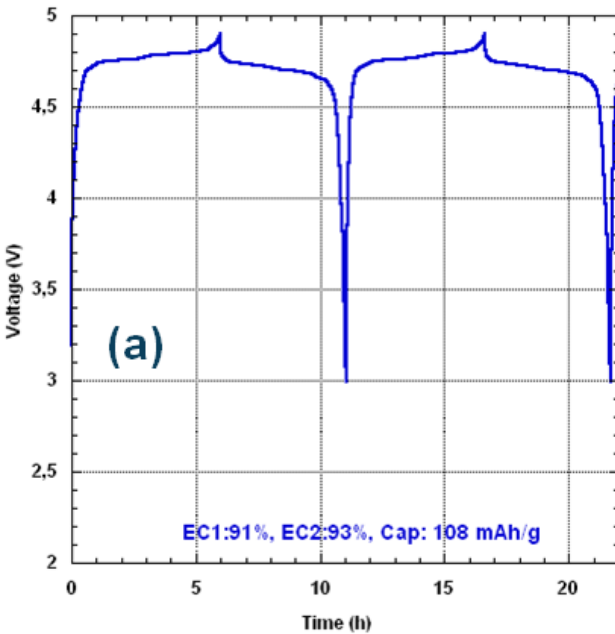


(c) Solid State (SS) sample

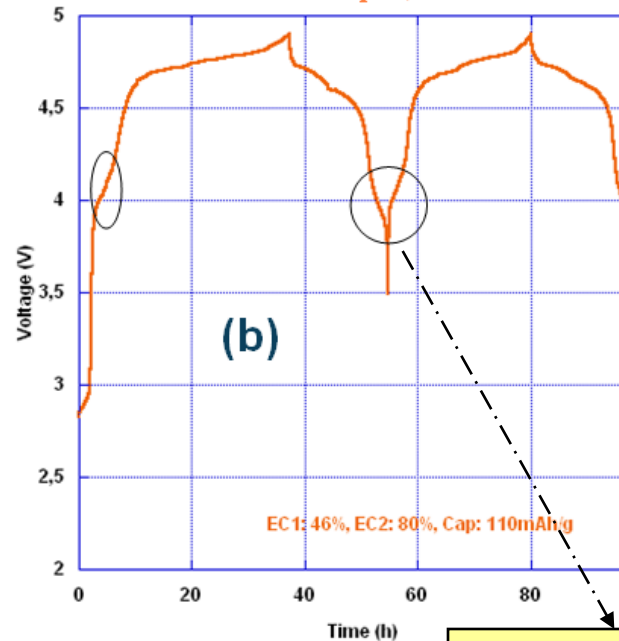
Particle size: SS > CP > company sample

# HQ Synthesis of $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$ : Formation

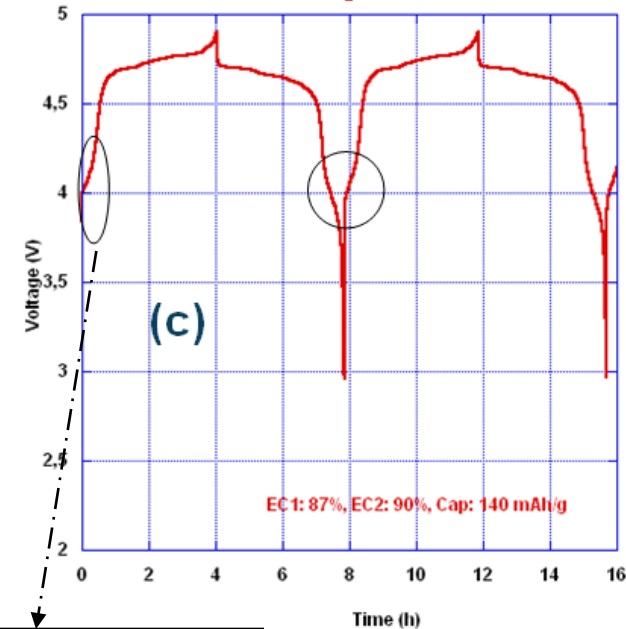
Company A, C/12



CP sample, C/24



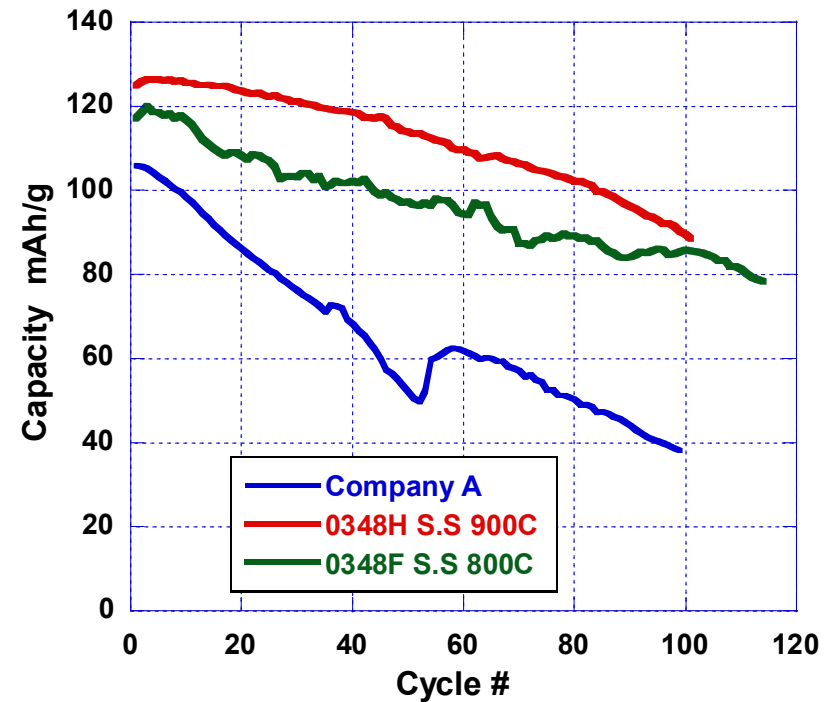
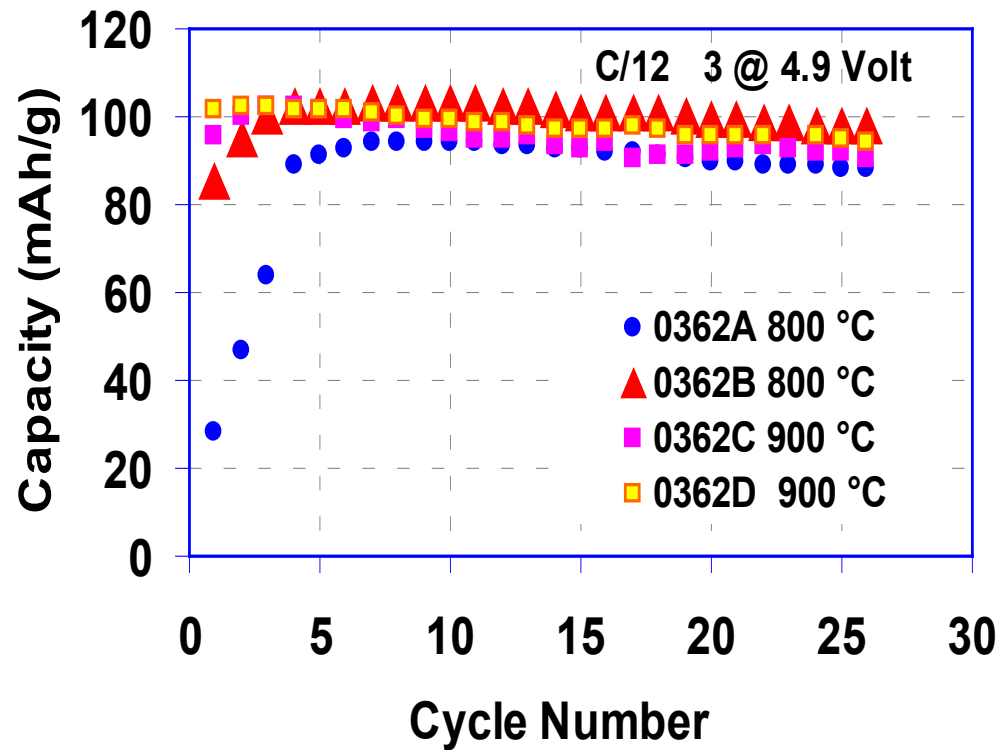
SS sample, C/4



$\text{Mn}^{4+} / \text{Mn}^{3+}$  redox couple

The oxygen deficiency under high annealing temperature resulted in the  $\text{Li}_{1-x}\text{-Ni}_x\text{-O}$  impurities ( $2\theta = 38^\circ$  and  $45^\circ$  in XRD) as well as small amount of reduced  $\text{Mn}^{3+}$  ( $\text{Mn}^{4+}/\text{Mn}^{3+}$ ) redox couple shows voltage plateau at 4.1 V).

# HQ Synthesis of $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$ : Cycling

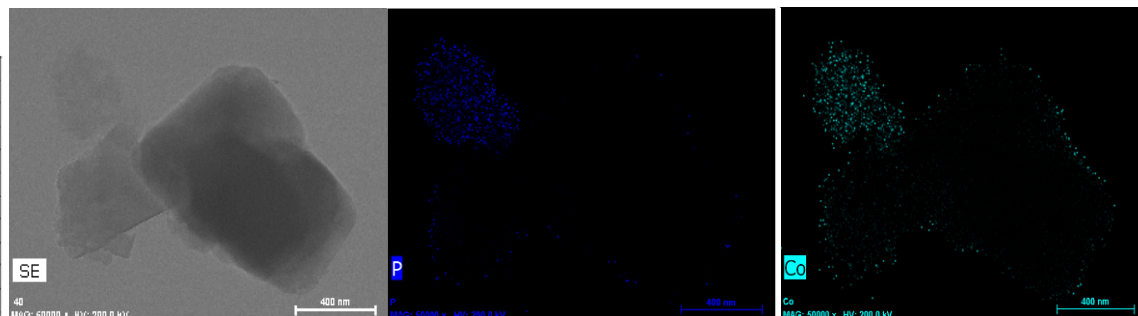
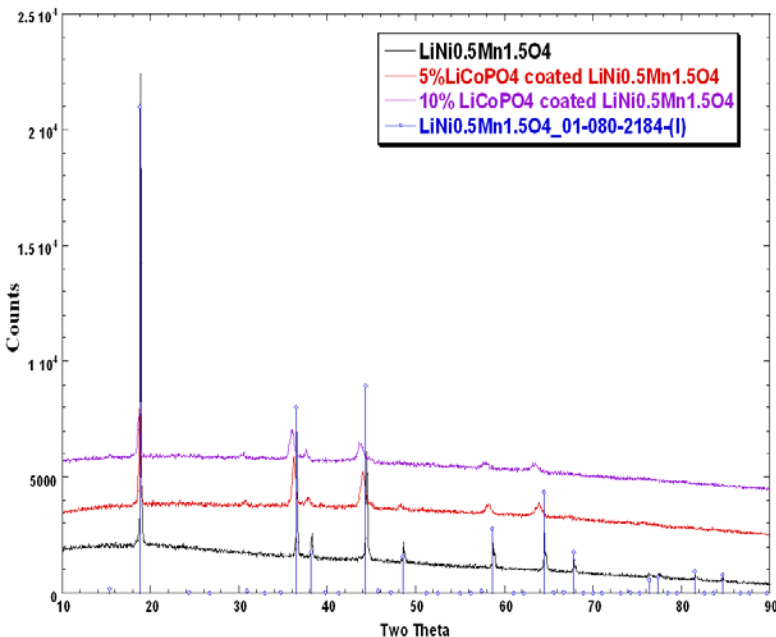


Materials synthesized at higher temperature show improved results

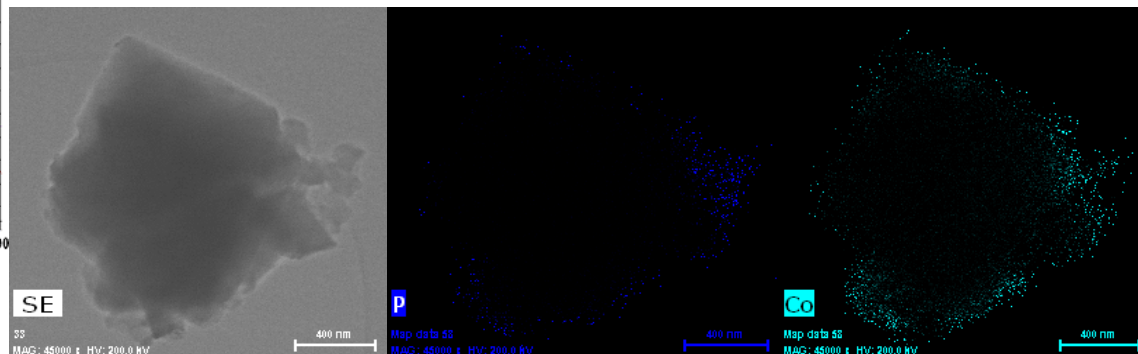
# $\text{LiCoPO}_4$ -Coated $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$

## 1 wt.% $\text{LiCoPO}_4$ coated-LNM

### $\text{LiCoPO}_4$ coated LNM in Ar



## 5 wt.% $\text{LiCoPO}_4$ coated-LNM



With traditional sol-gel method, no obvious impurities were detected in  $\text{LiCoPO}_4$ -coated LNM, but the diffraction peaks shift to lower angles, indicating the lattice parameters change after coating, probably some of the  $\text{Mn}^{4+}$  were reduced to  $\text{Mn}^{3+}$  in Ar.

# Summary

## □ Si Based Anode

- The C-SiO<sub>x</sub>-graphite based anode with the polyacrylonitrile butadiene binder showed a reversible capacity of 972mAh/g and 1st coulombic efficiency of 80%, and quite stable cycling capacity at C/6.
- The effect of the binder on the (SiO<sub>x</sub>: Gr (1:1)) anode performance is the following:  
Reversible Capacity: Polyimide > polyacrylonitrile butadiene > SBR > PVDF  
1<sup>st</sup> coulombic efficiency: SBR > polyimide = polyacrylonitrile butadiene > PVDF
- *In-situ* studies of the SiO<sub>x</sub> anode showed evidence that the larger particles (~ 13μm) start to crack at about 0.1V, but the smaller particles (< 2μm) are stable. Also some fissures were observed and the particles delaminate.
- Si-nano material based anode with the polyimide binder showed a reversible capacity of 1150mAh/g and 1st coulombic efficiency of 50%.

## □ Spinel LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub> Cathode Material

- Trace impurities observed in HQ-synthesized LMN samples; higher temperature leads to better crystallization with disordered structure. The highest reversible capacity obtained was 140mAh/g.
- C-LiFePO<sub>4</sub> nano-particles were coated on the LMN surface using a dry process, and promising results were obtained at 1C rate.
- LiCoPO<sub>4</sub> coating in argon does not change the bulk structure of LMN, but some Mn<sup>4+</sup> may be reduced to Mn<sup>3+</sup>.
- Developing in-situ SEM and TEM tools for the anode and cathode materials.
- Evaluation of 18650 cells fabricated at HQ was started.

# Future Activities

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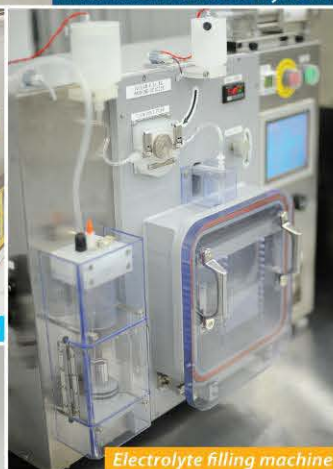
- ❑ **Remainder of this year**
  - **Continue evaluation of mixed graphite-SiO<sub>x</sub> and nano-Si as an alternative anode.**
  - **Continue improving the performance of the HQ-synthesized LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub> cathode for high energy, and send the optimized samples to PIs in the BATT Program for evaluation.**
  - **Continue exploring surface stabilization of the high-voltage LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub> cathode.**
  - **The successful *in-situ* SEM studies on the anode has encouraged us to continue studies on the Si and SiO<sub>x</sub> with different binders, and to investigate the surface of LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub> cathodes.**
  - **Evaluate high-voltage stable electrolytes with LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub> cathode.**
  - **The 18650 cells fabricated at HQ show promising results that will be helpful to other BATT investigators who want to take advantage of the HQ coating, calendaring equipment and cell assembly facilities.**
  - **Fabricate and test 18650 cells with oxide-LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub> cathodes and SiO<sub>x</sub>/graphite anodes, and provide cells to investigators in the BATT program for evaluation.**
- ❑ **All milestones completed**



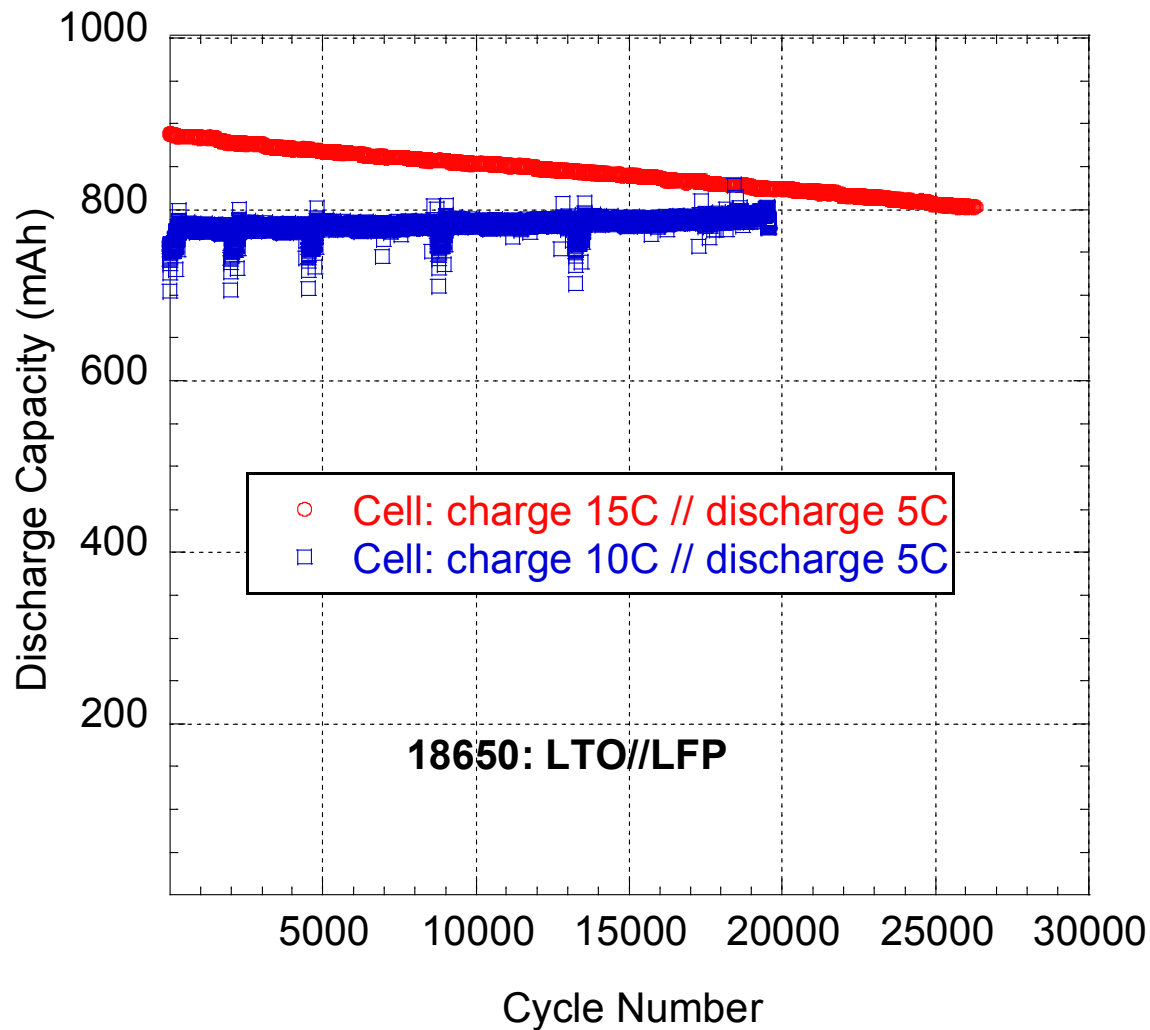
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# Technical Back-up Slides

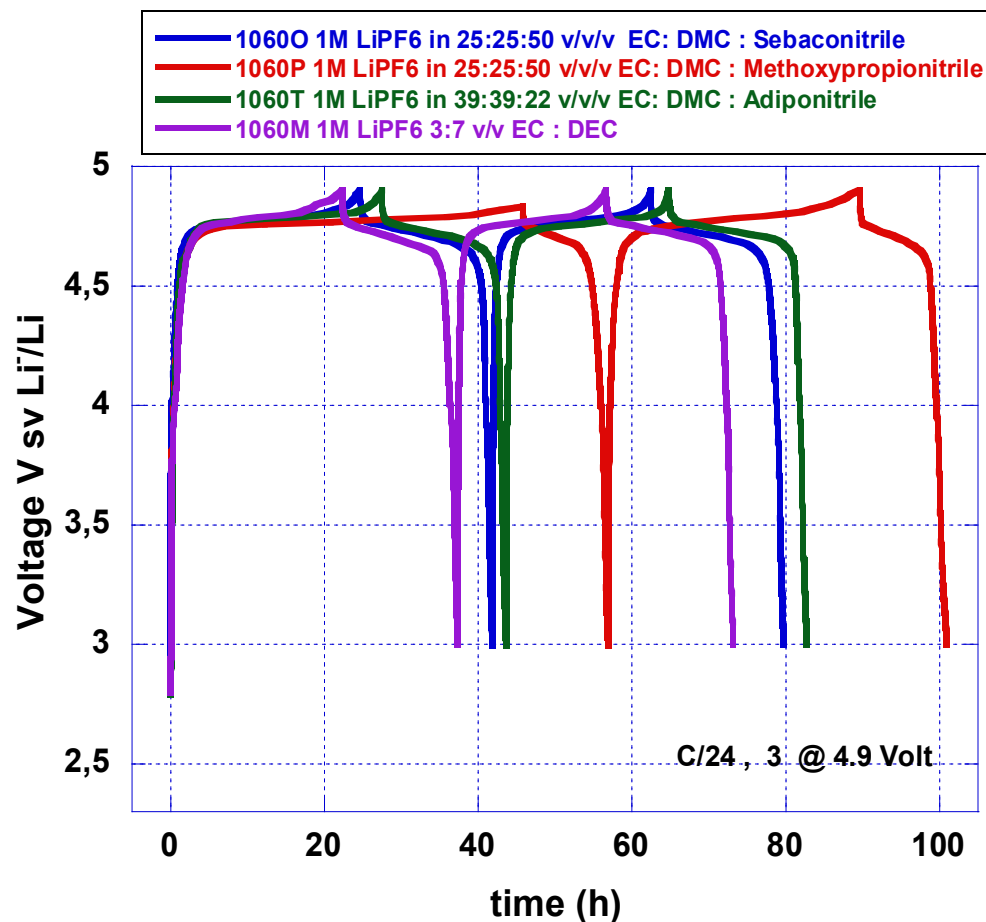
## Installation for fabrication of 18650 cylindrical cells



# 18650 Cells LTO/LFP



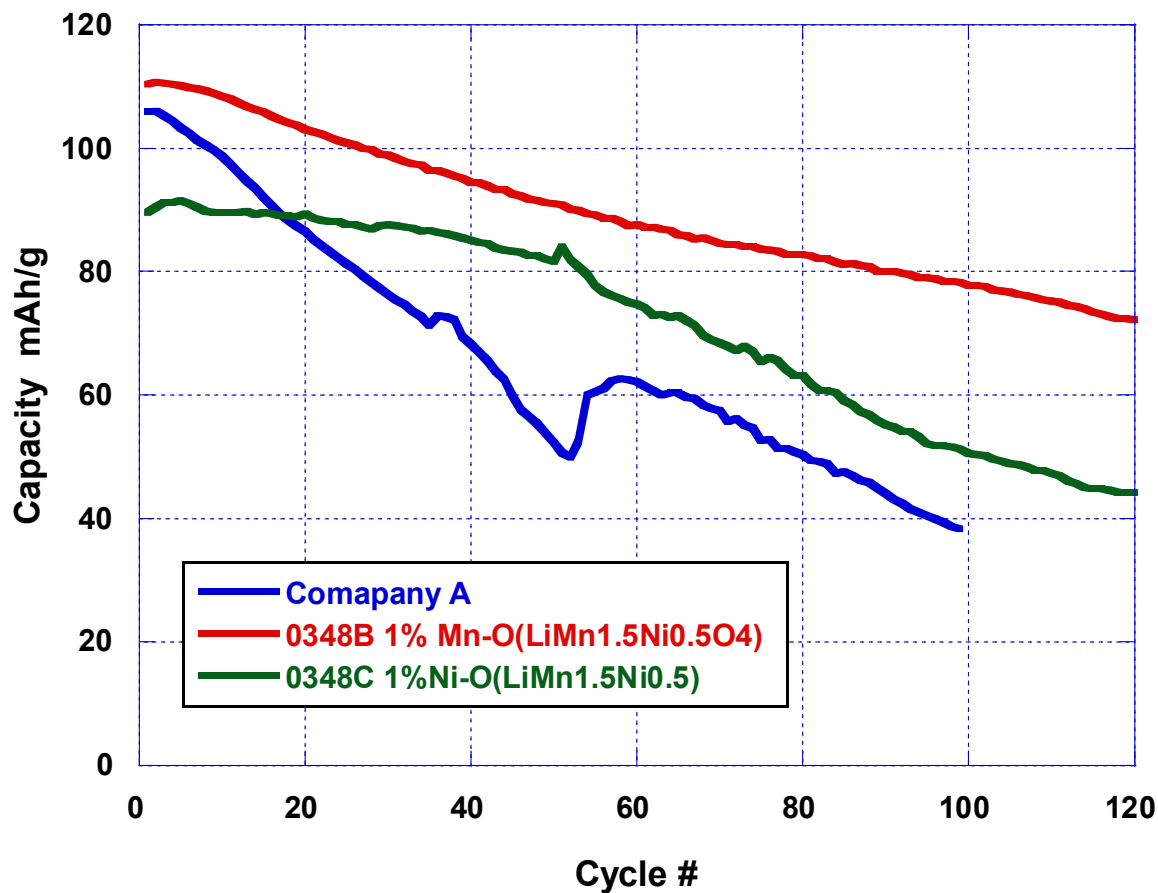
# Electrolytes Stable at High voltage



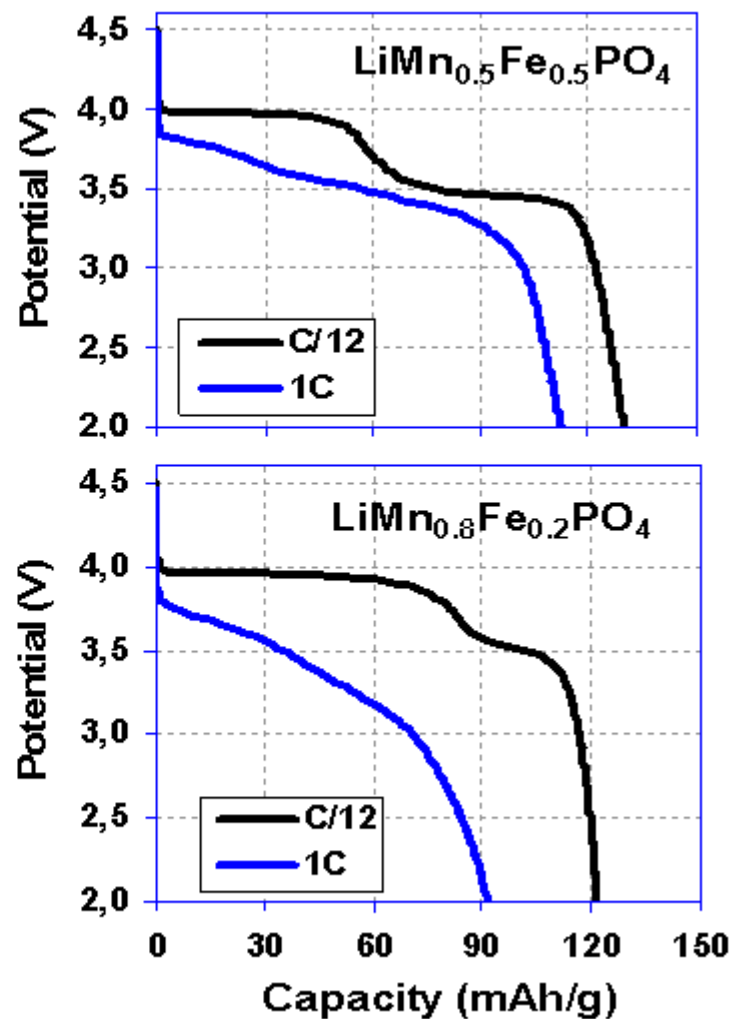
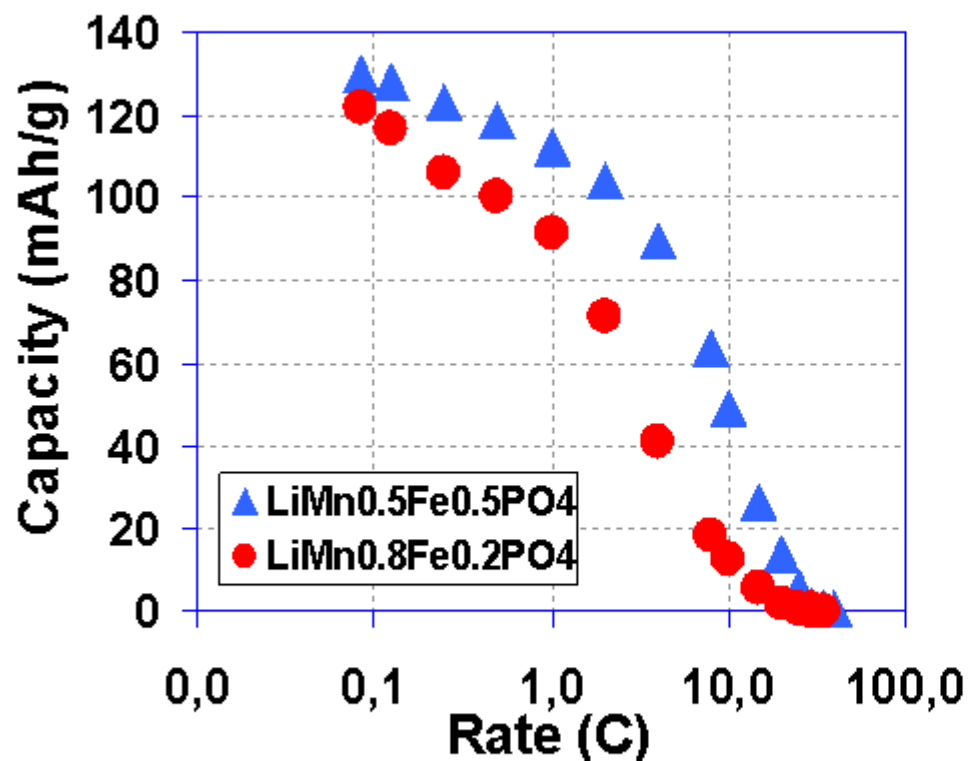
Electrolyte Configuration	1st EC (%)	Rev. Cap. (mAh/g)
1M LiPF <sub>6</sub> in 25:25:50 v/v/v EC: DMC : Sebaconitrile	70	111
1M LiPF <sub>6</sub> in 25:25:50 v/v/v EC: DMC : Methoxypropionitrile	24	73
1M LiPF <sub>6</sub> in 39:39:22 v/v/v EC: DMC : Adiponitrile	59	116
1M LiPF <sub>6</sub> 3:7 v/v EC : DEC	67	104

-The best charge-discharge performance was obtained during the formation cycles with an electrolyte containing Sebaconitrile as additive.

# Oxide-coated $\text{LiMn}_{3/2}\text{Ni}_{1/2}\text{O}_4$ :

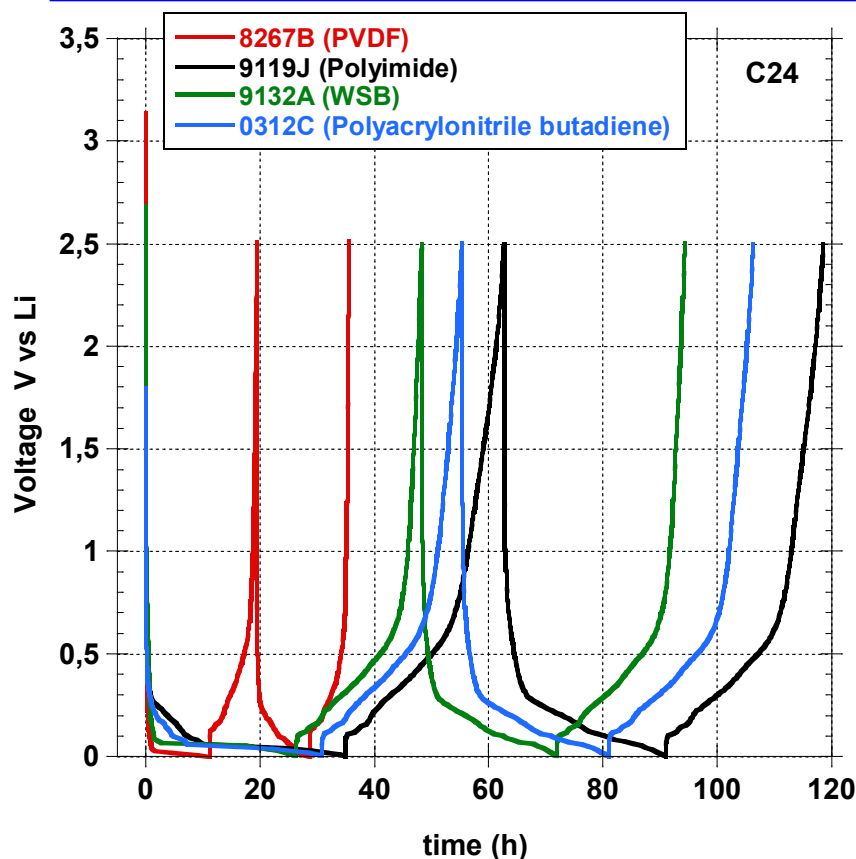


# $\text{LiMn}_{(1-x)}\text{Fe}_x\text{PO}_4$ Cathode Material



-The substituted  $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$  suffers at high rates, and the composition limit for power application should not exceed Mn content of 0.5.

# (SiO<sub>x</sub>+ Graphite (1:1)) Anode: Binder Effect



Li coin type cell  
1M LiPF<sub>6</sub>-EC-DEC+2%VC

Discharge/Charge: C/24  
T=25°C

	PVDF			WSB			Polyimide			polyacrylonitrile butadiene		
	Capacity (mAh/g)		Eff. (%)	Capacity (mAh/g)		Eff. (%)	Capacity (mAh/g)		Eff. (%)	Capacity (mAh/g)		Eff. (%)
	Discharge	Charge		Discharge	Charge		Discharge	Charge		Discharge	Charge	
Cycle 1	642	472	74	995	843	85	1332	1067	80	1177	941	80
Cycle 2	541	394	73	904	861	95	1085	1058	98	984	972	99